Supplemental Information for:

Oxy-Functionalization of Nucelophilic Re(I) Metal Carbon Bonds Catalyzed by Se^{IV}

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General Considerations: All air and water sensitive procedures were carried out either in a Vacuum Atmosphere glove box under argon, or using standard Schlenk techniques under argon. Labeled solvents, D_2O and CD_3CN were purchased from Cambridge Isotopes and used without further purification. CD_3CN was dried over CaH_2 and distilled for NMR used for compound characterizations. 2,2'-bipyridine (Lancaster Synthesis, Inc. 99+%) was sublimed at 100-120°C and stored under argon prior to use. CO_5ReBr and rhenium carbonyl ,$Re_2(CO)_{10}$, were purchased from Strem. THF (Mallinckrodt) was refluxed over Na/benzophenone and distilled under argon before use in synthesis or for column chromatography. Basic alumina (EMD) was dried for 2 days at 100°C in a vacuum oven, and then kept in the glove box antechamber under vacuum overnight before use. 48% aqueous HBr, GOLD LABEL SeO_2 (99.9+%), methaneseleninic acid ($CH_3Se(O)OH$, 95%), CH_3MgI (Grignard, 3.0M in diethyl ether), CH_3I (95.5% stabilized with Cu) and 4,4´-Dimethoxy-2,2´-bipyridine were all purchased from Aldrich, degassed and stored under argon. $^{13}CH_3I$ was purchased from Cambridge Isotopes, degassed, and stored under argon. CH_3I was vacuum transferred and stored over molecular sieves. GC/MS analysis was performed on a Shimadzu GC-MS QP5000 (ver. 2) equipped with cross-linked methyl silicone gum capillary column (DB5). The retention times of the products were confirmed by comparison to authentic samples. NMR spectra were obtained on a Varian Mercury-400 MHz and a Bruker 400MHz spectrometer at room temperature. All chemical shifts are reported in units of ppm and referenced to the residual protonated solvent. Standard C,H,N elemental analysis was performed by Desert Analytics Laboratory in Tucson, AZ. Fast atom bombardment (FAB) high resolution mass spectra were collected by the University of California, Riverside Mass Spectrometry facility. DIP-CI high resolution mass spectra were collected by the University of Florida, Gainesville, Florida Mass Spectrometry facility. IR Spectra were recorded on a Perkin-Elmer Spectrum One FTIR Spectrometer.

Synthesis of $(CO)_5ReCH_3$: 2.0 g rhenium carbonyl, $Re_2(CO)_{10}$, were dissolved in ~10mL dry THF under argon atmosphere in the glove box. This solution was transfer to a vial containing 10 gram Na/Hg amalgam and stirred for 2 hours, resulting in a deep red solution. The resultant solution was decanted from the amalgam and to it added 50-100 equivalents of CH_3I. After stirring for 45 minutes, the solution was removed from the glove box. DI water was added to the solution until a white solid ($(CO)_5ReCH_3$) precipitated. This solid was quickly filtered on a fine glass frit to remove bulk water, then transferred to a small vial for further drying over P_2O_5. Care must be taken, as

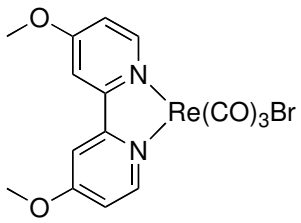
$(CO)_5ReCH_3$ is volatile. Extended vacuum drying will result in loss of compound. After drying over P_2O_5 in a sealed container was complete (15-20h), the compound can be further purified by sublimation at 60°C. Synthesis and characterization of this compound were previously reported[1] $(CO)_5Re^{13}CH_3$ was synthesized following the same procedure using $^{13}CH_3I$.

Synthesis for $(CO)_3$(Bpy)Re(I)Br/$(CO)_3$(4,4´-Bismethoxy-2,2´bipyridine)Re(I)Br: A 50 mL Schlenk tube with a reflux condenser was charged with 1.0 g (2.43 mmol) of $(CO)_5$ Re(I)Br, 1.2eq (0.455 g; 2.91 mmol) of 2,2'-bipyridine (or 0.629g; 2.91mmol of 4,4´-Bismethoxy-2,2´bipyridine respectively), and 15 mL of toluene with a magnetic stirring bar under an argon atmosphere vented to a bubbler (THF can be used for the reaction as well; however, this method often leads to lower reaction yields). The flask was placed in a well-stirred oil bath (120°C) for 2 hours. In 15 minutes, the reaction solution had turned from colorless to yellow with a bright yellow precipitate. After 2 hours, the flask was removed from the oil bath and cooled to room temperature and a yellow solid was collected by filtration on a glass filter frit followed by washing with cold diethyl ether. The insoluble yellow fine powder was recovered as the title compounds in more than 95% yield in both cases.

Rhenium-(2,2´bipyridine)-triscarbonyl-bromide

The synthesis and characterization of this compound was previously reported.[2]

Rhenium-(4,4´-bismethoxy-2,2´bipyridine)-triscarbonyl-bromide



^{1}H-NMR (DMSO-d_6, 400MHz): δ= 4.06 (s, 6H), 7.30 (dd, *J*= 2.6, 6.5 Hz, 2H), 8.34 (d, *J*= 2.6 Hz, 2H), 8.76 (d, *J*= 6.5 Hz, 2H).
^{13}C-NMR (DMSO-d_6, 100MHz): δ= 57.02, 111.00, 113.53, 154.14, 157.02, 167.77, 190.25, 197.63.
IR(Ge): ν[cm^{-1}] = 3067, 2941, 2016(CO), 1875(CO), 1849(CO), 1614, 1560, 1490, 1461, 1438, 1414, 1330, 1312, 1269, 1254, 1230, 1047, 1031, 1009, 897, 841, 826.
HRMS (DIP-CI): calcd. for $C_{15}H_{12}N_2O_5ReBr$: 563.9459, found: $[M]^+$ 563.9457 (Mass Error -0.3809ppm)
MS (DIP-CI): 566 $[M]^+$, 538 $[M\text{-}CO]^+$, 487 $[M\text{-}Br]^+$.

General synthesis of $(CO)_3$(bpy)Re-alkyl: $(CO)_3$(bpy)ReBr was suspended in dry THF (conc. 0.05mol/L) and treated with 1.5eq of the corresponding Grignard reagent (MeMgI, 3.0M in Et_2O; EtMgBr, 1.0M in THF; n-PrMgBr, 1.0M in THF) at room temperature. The reaction was stirred for 1h and a clear red solution formed. Decomposition results at

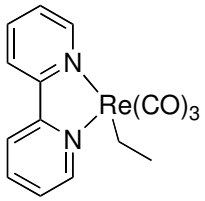
longer reaction times with excess Grignard, possibly due to reduction or substitution of the bpy ligand. Immediately following reaction, the THF solution was run through a plug of dry neutral or basic alumina and the orange product eluted with THF. Solvent was evaporated, leaving analytically pure $(CO)_3$(bpy)Re-alkyl. Evidence of unreacted starting material, or possibly hydrolyzed $(CO)_3$(bpy)Re-alkyl (to form presumably $(CO)_3$(bpy)Re(OH) or variants) can be noted as a faint yellow, slowly eluting band at the top of the alumina plug. Typical yields were between 70-90% based on $(CO)_5$ReBr.

Rhenium-(2,2'-bipyridine)-triscarbonyl-methyl

The synthesis and characterization of this compound was previously reported[3]

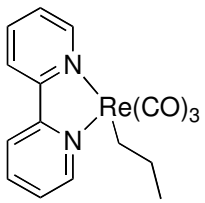
Elemental analysis: Expected, C, 38.09 H, 2.51 N, 6.35. Found, C, 37.98 H, 2.62 N, 6.09.

Rhenium-(2,2'-bipyridine)-triscarbonyl-ethyl



^{1}H-NMR (CD_2Cl_2, 400 MHz): δ = -0.29 (q, *J* = 7.8 Hz, 2H), 1.22 (t, *J* = 7.8 Hz, 3H), 7.50 (ddt, *J* = 1.2, 5.5, 7.6 Hz, 2H), 8.08 (tt, *J* = 1.4, 8.1 Hz, 2H), 8.39 (d, *J* = 8.2 Hz, 2H), 9.01 (d, *J* = 5.5 Hz, 2H).
^{13}C-NMR (CD_2Cl_2, 100 MHz): δ = 16.58, 18.06, 122.53, 125.70, 136.58, 151.88, 154.10, 192.20, 204.33.
IR(Ge): ν[cm^{-1}] = 2851, 2791, 1976(CO), 1845(br, 2CO), 1602, 1469, 1443, 1314, 1157, 758, 730.
HRMS (DIP-CI): calcd. for $C_{15}H_{14}O_3N_2Re$: 455.0534; found $[M+H]^+$: 454.0419 (Mass Error = 1.1031 ppm).
MS (DIP-CI): 881$[2M-C_2H_5]^+$, 457$[M+H]^+$, 427$[M-C_2H_5]^+$+$[M-CO]^+$, 157.

Rhenium-(2,2'-bipyridine)-triscarbonyl-propyl

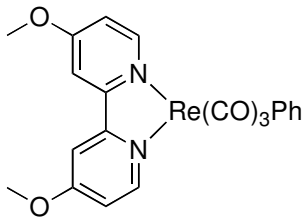


^{1}H NMR (CD_3CN, 400 MHz) δ = -0.31 (t, *J* = 8.3 Hz, 2H), 0.66 (t, *J* = 7.3 Hz, 3H). 1.48 (m, 2H), 7.51 (ddt, *J* = 1.3, 2.2, 6.8 Hz, 2H), 8.08 (tt, *J* = 1.1, 8.2 Hz, 2H), 8.40 (d, *J* = 8.1 Hz, 2H), 9.02 (d, *J* = 5.6 Hz, 2H).

^{13}C NMR (CD_3CN, 100 MHz) δ = 22.71, 29.66, 31.71, 125.19, 127.99, 139.25, 153.66, 155.98, 194.18, 206.15.
IR(Ge): ν[cm^{-1}] = 2941, 2856, 2778, 1977 (CO), 1845 (CO), 1601, 1469, 1443, 1312, 1067, 759, 730.
HRMS (DIP-CI): calcd. for $C_{16}H_{16}O_3N_2Re$: 468.0612; found $[M]^+$: 468.0581

Synthesis of $(CO)_3$Re(4,4´-Bismethoxy-2,2´bipyridine)phenyl: A Schlenk flask is charged with 563mg (1mmol) of Re(4,4´-bismethoxy-2,2´-bipyridine)$(CO)_3$Br and 20mL dry THF. The Re complex is dissolved by heating gently. After cooling to r.t., the solution is treated with 2 eq PhMgBr (1.0M in THF, 2mL) and the reaction is stirred for 14h under the exclusion of light. After full conversion the reaction mixture is concentrated to 5 mL and filtered over a patch of neutral Alumina in a Schlenk frit. The filtrate is concentrated to 2 mL and the complex precipitated by addition of cold dry diethylether to yield an orange solid.

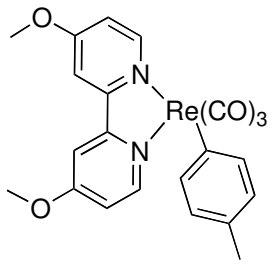
Rhenium-(4,4´-bismethoxy-2,2´bipyridine)-triscarbonyl-phenyl



^{1}H-NMR (CD_3CN, 400 MHz): δ= 3.99 (s, 6H), 6.65-6.74 (m, 3H), 7.11-7.15 (m, 4H), 7.75 (d, *J*= 2.7 Hz, 2H), 8.90 (d, *J*= 6.5 Hz, 2H).
^{13}C-NMR (CD_3CN, 100 MHz): δ= 57.47, 110.94, 114.25, 123.18, 127.60, 129.27, 140.12, 154.48, 157.71, 168.25, 196.50, 203.50.
IR(Ge): ν[cm^{-1}] = 3046, 2970, 1985(CO), 1894(CO), 1849(CO), 1615, 1557, 1495, 1463, 1425, 1327, 1311, 1267, 1250, 1221, 1048, 1032, 1009, 875, 828, 736, 705, 699.
HRMS (DIP-CI): calcd. for $C_{21}H_{17}O_5N_2Re$: 562.0667; found $[M]^+$ 562.0667 (Mass Error: -0.1821ppm)
MS (DIP-CI): 564 $[M]^+$, 536 $[M\text{-}CO]^+$, 487 $[M\text{-}C_6H_5]^+$, 217.

Synthesis of $(CO)_3$Re(4,4´-Bismethoxy-2,2´bipyridine)tolyl: A Schlenk flask is charged with 140mg (0.25mmol) of Re(4,4´-bismethoxy-2,2´-bipyridine)$(CO)_3$Br and 8mL dry THF in a glove box. The Re complex is dissolved by heating gently. After cooling to r.t., the solution is treated with 2 eq 4-MethylphenylMgBr (0.5M in THF, 2mL) and the reaction is stirred for 1h under the exclusion of light. The solution turns form yellow to deep red and is filtered over a small patch of neutral Alumina. The solvent is removed in vacuo to yield an orange solid in 62% yield.

Rhenium-(4,4´-bismethoxy-2,2´bipyridine)-triscarbonyl-(4-methylphenyl)



^{1}H-NMR (400 MHz; CD_3CN): δ = 2.47 (s, 3H), 4.00 (s, 3H), 6.56 (d, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 7.9 Hz, 1H), 7.12 (m, 1H), 8.89 (d, *J* = 6.4 Hz, 1H), 7.77 (d, *J* = 2.7 Hz, 1H),
^{13}C-NMR (CD_2Cl_2, 100 MHz): δ= 20.14, 55.95, 109.30, 111.90, 127.25, 130.72, 138.61, 153.19, 156.06, 163.95, 166.36, 194.96, 202.15.
IR(Ge): ν[cm^{-1}] = 3330, 2983, 1988(CO), 1885(CO), 1861(CO), 1609, 1558, 1489, 1464, 1335, 1252, 1221, 1045, 1031, 795.
HRMS (DIP-CI): calcd. for $C_{21}H_{19}N_2O_5Re$ $[M\text{-}CO]^+$: 548.0874; found $[M\text{-}CO]^+$: 548.0909 (Mass Error = 6.3168 ppm; Spectral Accuracy: 89.5%).
MS (DIP-CI): 578$[M]^+$, 566, 550$[M\text{-}CO]^+$, 538.

Synthesis of $(CO)_3Re(bpy)OSe(O)OCH_3$: 50 mg (0.113 mmol) $(CO)_3(bpy)ReCH_3$ was dissolved in 7.5 mL CH_3CN and treated with 13.0 mg SeO_2(0.113 mmol) and 0.05 mL H_2O under air. The reaction turns pale yellow and forms a precipitate. It was stirred overnight (~12 h). 3 mL diethyl ether was added to further precipitate the compound. The precipitate was collected on a frit, washed thoroughly with water and ether and dried on a vacuum line (~10 mTorr) for 24 hours.

Rhenium-(2,2'-bipyridine)-triscarbonyl-methylselenite

^{1}H-NMR (400 MHz; CD_2Cl_2): δ 2.03 (s, $J^{Se\text{-}H}$=7Hz, 3H), 7.50 (dddd, *J* = 7.6, 5.5, 3.4, 1.3 Hz, 2H), 8.06 (tt, *J* = 1.3, 8.2Hz, 2H), 8.16 (dd, *J* = 8.2, 0.8 Hz, 2H), 8.98 (ddd, *J* = 5.5, 1.6, 0.8 Hz, 2H).
^{13}C-NMR (MeOD, 100 MHz): δ = 44.99, 123.64, 123.70, 127.47, 127.61, 139.96, 139.99, 153.59, 153.67, 156.12, 156.15.
The ^{13}C-NMR of this compound shows an asymmetric bipyridine ligand, suggesting a *mer*-isomer. It is not clear if this is the direct product of the reaction or if isomerization occurs in solution. The carbonyl signals could not be detected in the ^{13}C-NMR spectrum, but were clearly visible by IR.
IR(Ge): ν[cm^{-1}] = 3219, 2005(CO), 1922, 1878(CO, br), 1602, 1475, 1447, 1400, 1317, 1248, 1163, 825, 772, 741, 727.
Elemental analysis: Expected, C, 30.44; H, 2.01; N, 5.07. Found, C, 30.03; H, 1.83; N, 5.23.

Synthesis of $(CO)_3Re(bpy)OSeO_2H$: 50mg (0.113mmol) $(CO)_3(bpy)ReCH_3$ was dissolved in 7.5 mL 9:1 CH_3CN:H_2O and treated with ~100 mg SeO_2(excess). The

reaction turns yellow and starts to precipitate solid immediately. A fine yellow solid was collected on a glass frit by vacuum filtration, washed with water, acetonitrile, and ether and dried under vacuum for 24 hours.

Rhenium-(2,2'-bipyridine)-triscarbonyl-biselenite

^{1}H-NMR (400 MHz; MeOD): δ= 7.72 (ddd, *J* = 7.7, 5.5, 1.3 Hz, 2H), 8.28 (td, *J* = 7.9, 1.6 Hz, 2H), 8.60 (dt, *J* = 8.2, 0.9 Hz, 2H), 9.08 (d, *J* = 5.4 Hz, 2H).
^{13}C-NMR (MeOD, 100 MHz): δ = 125.16, 128.65, 141.66, 145.53, 157.49, 193.07, 198.13.
IR(Ge): ν[cm^{-1}] = 3084, 2376, 2006(CO), 1921, 1877(CO, br), 1739, 1603, 1474, 1446, 875, 773, 753, 730, 666.
Elemental analysis: Expected, C, 28.16; H, 1.64; N, 5.05. Found, C, 28.57; H, 1.41; N, 5.16

$(CO)_5ReCH_3$ reactions with O-atom donors: 30.0 mg ($8.79 \cdot 10^{-2}$ mmol) $(CO)_5ReCH_3$ and $2.64 \cdot 10^{-1}$ mmol (3 equivalents) of O-atom donor (PhIO, KIO_4, or PyO) were heated under air at 100 °C in a CD_3CN/D_2O solvent system (9:1 for PhIO and PyO, 8:2 for KIO_4) in an 8" J-Young NMR tube for 2 hours. Yields were measured by integration of the product resonance to a cyclohexane or benzene external standard contained in a flame sealed capillary tube.

$(CO)_5ReCH_3$ reactions with Pd and Cu salts: 30.0 mg ($8.79 \cdot 10^{-2}$ mmol) $(CO)_5ReCH_3$ and 3 equivalents of Pd or Cu salt ($Pd(OAc)_2$, $Cu(OTf)_2$) were heated under air or under argon at 100 °C in a 9:1 CD_3CN/D_2O solvent system for 15 hours. No methanol was observed in these reactions.

$(CO)_5ReCH_3$ and $(CO)_5Re^{13}CH_3$ reaction with D_2SeO_3: 30.0 mg ($8.79 \cdot 10^{-2}$ mmol) $(CO)_5ReCH_3$ or $(CO)_5Re^{13}CH_3$ and 9.8 mg ($8.79 \cdot 10^{-2}$ mmol) SeO_2 were heated under air at 100 °C in a 9:1 CD_3CN/D_2O solvent system for 2 hours. Yields were measured by integration of the CH_3-SeO_2H product resonance to a cyclohexane or benzene external standard contained in a flame sealed capillary tube.

Catalytic reaction of $(CO)_5ReCH_3$ with SeO_2 and KIO_4: 30.0 mg ($8.79 \cdot 10^{-2}$ mmol) $(CO)_5ReCH_3$, 60.0 mg ($2.61 \cdot 10^{-1}$ mmol, 3 equivalents) KIO_4, and 1.1 mg (0.1 equivalent, catalytic) SeO_2 were heated under air at 100 °C in a 8:2 CD_3CN/D_2O solvent system (to increase solubility of KIO_4) in an 8" J-Young NMR tube for 15 hours. Yields were measured by integration of the product resonance to a cyclohexane or benzene external standard contained in a flame sealed capillary tube

Reaction of $(CO)_3Re(bpy)CH_3$ with SeO_2: In a J-Young NMR tube with reseable Teflon valve, 5 mg of $(CO)_3Re(bpy)Me$ and 0.5 mL of a 9:1 CD_3CN/D_2O mixture were added in the presence and absence of light (all reactions carried out in dark were in amberized glassware wrapped in dark fabric). Then 10 eq of SeO_2 were added under air and the NMR tube shaken. Following reaction with SeO_2, excess $NaIO_4$ (~10 eq) was added and the NMR tube heated over night at 100°C. Each step was monitored by ^1H NMR.

Reaction of $(CO)_3Re(byp)alkyl$ with SeO_2 and oxidation to the corresponding alcohol: 5mg of the $(CO)_3Re(byp)alkyl$ complex are dissolved in 0.4mL dry CD_3CN in a J-Young NMR tube, equipped with an external coaxial standard (1,3,5-trimethoxybenzene in C_6D_6). 2eq of SeO_2 in 0.05mL of D_2O are added to the NMR tube and upon mixing a color change of the solution from orange to yellow is observed. 2 eq of $NaIO_4$ are added and the reaction is heated over night at 100°C. The alcohol products are determined by comparison of the product NMR spectra to known NMR data.

Reaction of $(CO)_3Re(4,4´$-bismethoxy-2,2´-bipyridine)aryl complexes with SeO_2: 5mg of the $(CO)_3Re(4,4´$-bismethoxy-2,2´-bipyridine)aryl complex are dissolved in 0.4mL dry CD_3CN in a J-Young NMR tube, equipped with an external coaxial standard (1,3,5-trimethoxybenzene in C_6D_6). 2eq of SeO_2 in 0.05mL of D_2O are added to the NMR tube and upon mixing a color change of the solution from orange to yellow is observed. The seleninic acid products are determined by comparison of the product NMR spectra to known NMR data.

Control reactions of CH_3SeO_2H with KIO_4 in aqueous media: 5.0 mg CH_3SeO_2H ($3.9 \cdot 10^{-2}$ mmol) and 90.6 mg ($3.9 \cdot 10^{-1}$ mmol, 10 equivalents) were heated under air in 9:1, 8:2, and 1:1 CD_3CN/D_2O solutions as well as neat D_2O for 12 hours to verify that methanol could be produced. Trace methanol was observed for the 9:1 solvent system, but increasing water concentration resulted in yields of >90% methanol as measured by integration of the methanol C*H*$_3$- resonance to a cyclohexane or benzene external standard contained in a flame sealed capillary tube.

Reaction of $bpy(CO)_3ReCH_3$ with D_2O: The protic stability of $bpy(CO)_3ReCH_3$ was measured by treating a CD_3CN solution of ~5 mg of the complex with ~0.1 mL D_2O. The solution immediately starts to change from the distinct orange (methyl complex) to yellow with simultaneous precipitation of material. CH_3D was confirmed as a product by GC/MS analysis on a hydrocarbon Gas-Pro column. The resulting ^1H NMR spectrum showed the presence of at least 2 new sets of pyridyl resonances, though the integration of these peaks referenced to an external standard accounted for less than 25% of the original material. Detailed kinetics of the protonation reaction were not undertaken, but are currently being studied for all of the bipyridine ligated complexes. This reactivity with water precluded studying $bpy(CO)_3ReCH_3$ under catalytic conditions similar to $(CO)_5ReCH_3$.

Kinetic analysis of $(CO)_5ReCH_3$ + D_2SeO_3 reaction in 9:1 CD_3CN:D_2O: Stock solutions of $(CO)_5ReCH_3$ and H_2SeO_3 in 9:1 CD_3CN:D_2O were prepared in separate vials at 20.5mM and 0.205M, respectively so that the concentration of D_2SeO_3 was pseudo-first order throughout the reaction with respect to the Re reactant. A ^1H NMR spectrum of 0.25mL CO_5ReCH_3 solution was taken prior to reaction in an 8" J-Young NMR tube sealed with a Teflon cap and outfitted with a benzene/CCl_4 co-axial external standard (sealed capillary supported by one fitted Teflon O-ring). Precisely 0.25mL D_2SeO_3 solution was then added and another ^1H NMR spectrum was taken as the t=0. The production of CH_3SeO_2H at ~2.6 ppm was monitored along with the disappearance of the Re-CH_3 resonance at -0.26 ppm by heating the NMR tubes in the probe. Reactions were run in triplicate at 50, 60, 70, and 80°C in order to perform the Eyring analysis shown below.

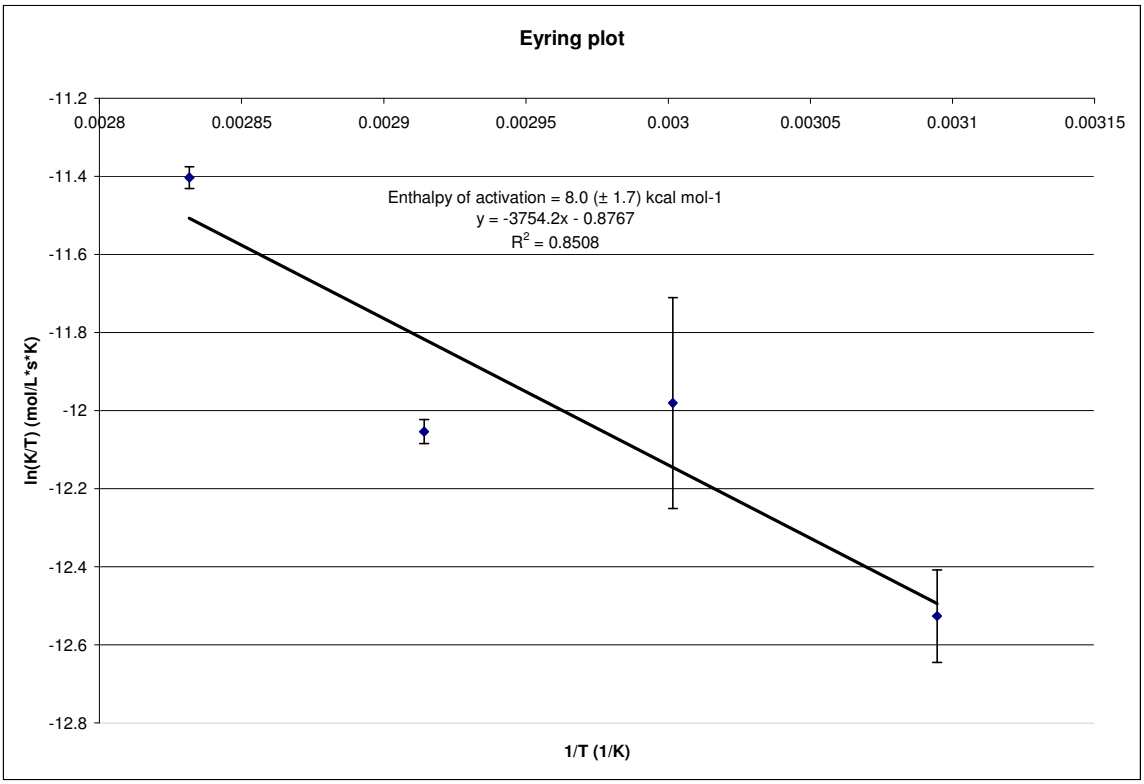


Figure S1.

CO inhibition study: 4.2 mg $(CO)_5ReCH_3$ was dissolved in 0.6mL of a 9:1 CD_3CN:D_2O solution containing ~100 equivalents of D_2SeO_3 in an 8" J-Young tube sealed with a Teflon cap. The reaction was blanketed with 1atm CO, resealed and shaken vigorously, then heated at 70°C in the NMR probe. The reaction was monitored by ^1H NMR until complete. The rate of reaction was unchanged in the presence of CO gas.

CH_3SeO_2H oxidations by iodine reagents: ***KIO_3*** - 5.0mg CH_3SeO_2H and 25.3mg KIO_3 were dissolved in 0.5mL D_2O in an 8" J-Young NMR tube and heated at 150°C for ~30 minutes. 21% conversion to methanol was observed at this short reaction time at δ 3.33 along with unreacted CH_3SeO_2H starting material at δ 2.78. ***I_2*** - 5.0mg CH_3SeO_2H was heated at 150°C for ~5 hours with 30.0mg I_2 in D_2O under argon. No reaction occurred. 10uL of degassed 40% KOD was added and the reaction was heated for 30 minutes at 150°C under argon. This yielded methanol in accordance with the known reaction of I_2 with OH^-:[4]

$$I_2 + 2OH^- \rightarrow I^- + IO^- + H_2O \quad (K_{eq}\sim 30) \qquad (1)$$

$$3IO^- \rightarrow 2I^- + IO_3^- \quad (K_{eq}\sim 10^{20}) \qquad (2)$$

KI - Heating 10.0mg CH_3SeO_2H with 30.0mg KI in 0.5mL D_2O at 150°C for 4 hours under argon resulted in no reaction. Addition of 10uL KOD and continued heating under argon for 5 hours resulted in no reaction as well. Opening the J-Young tube to air and reheating for 5 hours resulted in the formation of methanol as well as formaldehyde as monitored by ^1H NMR spectroscopy in accordance with the known air oxidation of I^-:

$$2I^- + O_2 \rightarrow I_2 \text{ (unbalanced)} \qquad (3)$$

This reaction likely proceeds with the formation of a reduced oxygen species such as H_2O_2 which would render the solution basic, i.e.:

$$2I^- + O_2 + H_2O \rightarrow I_2 + H_2O_2 + 2OH^- \qquad (4)$$

Accordingly, reaction of 5.0mg CH_3SeO_2H with 30.0mg of KI under air or 1atm O_2 in D_2O at 150°C for 6 hours yields methanol and formaldehyde. The oxygen species resulting from the air oxidation of I^- is most likely responsible for the overoxidation of CH_3SeO_2H to formaldehyde, as CH_3SeO_2H does not oxidize in the presence of air under the same conditions. I_2 is also known to be oxidized by H_2O_2:

$$I_2 + 5H_2O_2 \rightarrow 2HIO_3 + 4H_2O \qquad (5)$$

Computational Details: All calculations were performed with using the B3LYP hybrid density functional as implemented by the Jaguar 6.5 program package. For all atoms except selenium the LACV3P** basis set was used for geometry optimizations and solvation energies, and LACV3P**++ for single point gas phase energy corrections. For selenium the all electron basis set MSV augmented with one d-function was used for geometries and solvation energies (MSV+d), and MSV augmented with one d-function and one f-function used for the single point energy corrections (MSV+d,f). In MSV+d the d-function had an exponent α=0.5213. In MSV+d,f the additional d-function used α=0.4530, while the f-function had α=0.6850. With the additional d- and f-functions values in good agreement with experimental data for conversion of Se between different oxidation states were obtained. Solvation was modeled implicitly with the Poisson-Boltzmann solver (PBF) implemented in Jaguar. The parameters were set to e=36.6 and

probe radius=2.18 to simulate acetonitrile. Vibrational frequencies were calculated numerically including the PBF. The vibrational entropies were extracted from the solution phase frequency calculations, while the translational and rotational entropies were calculated in the gas phase and scaled by a factor of 0.5, which in our experience yields results in good agreement with experiments for solution phase entropies.

XYZ-coordinates in Å and energies.

$Re(CO)_5CH_3$

$E_{elctronic}$= -685.9789823567 a.u.
E_{solv}= -0.0053822 a.u.
ZPE= 48.584 kcal/mol
$\Delta H_{298.15}$= 9.11288 kcal/mol
$\Delta S_{vib\ 298.15}$= 44.423 cal/(mol K)
$\Delta S_{trans,rot\ 298.15}$= 37.3465 cal/(mol K)

Re1	-0.0010544160	-0.0472494336	-0.0010022568
O2	3.1380786927	-0.3185281196	0.0281484577
C3	2.0049314962	-0.1944401689	0.0171265749
O4	-0.0396258935	-0.3032027012	3.1389737190
C5	-0.0253381093	-0.1855418880	2.0050929572
O6	0.0192700408	3.0809015648	0.0044046050
C7	0.0088229479	1.9317591838	0.0020663897
O8	-3.1420736752	-0.2803168696	-0.0316423906
C9	-2.0073948744	-0.1689185160	-0.0210654967
O10	0.0212469346	-0.2904179137	-3.1417656455
C11	0.0135862209	-0.1754029101	-2.0075073432
C12	0.0208840581	-2.3487950296	0.0052189797
H13	-0.9777709970	-2.7517783259	0.1808812476
H14	0.3793632730	-2.7390398872	-0.9489091321
H15	0.6798489185	-2.7256403905	0.7901283023

H_2SeO_3

$E_{elctronic}$= -2626.13674273109
E_{solv}= -0.0232088
ZPE= 18.287 kcal/mol
$\Delta H_{298.15}$= 4.2009 kcal/mol
$\Delta S_{vib\ 298.15}$= 10.965 cal/(mol K)
$\Delta S_{trans,rot\ 298.15}$= 32.827 cal/(mol K)

Se1	1.2707845070	0.4928866478	0.1061707961
O2	0.3074944528	1.1783706000	1.2220162336
O3	0.1793035580	-0.5856207100	-0.8344680913
H4	-0.5711403984	-0.8895459265	-0.2919466453
O5	2.1832771134	-0.7669015564	1.0121762108

H6	1.6734374207	-1.0905758079	1.7772103299

$SeO_2(OH_2)$
$E_{elctronic}$= -2626.121521
E_{solv}= -0.0295176
ZPE= 18.214 kcal/mol
$\Delta H_{298.15}$= 4.2010 kcal/mol
$\Delta S_{vib\ 298.15}$= 11.119 cal/(mol K)
$\Delta S_{trans,rot\ 298.15}$= 33.1355 cal/(mol K)

Se1	-1.5085155729	-1.0483449878	0.0891943415
O2	-2.4532547075	-0.0191205030	-0.7405046266
H3	0.9925176421	-1.2632001503	-1.5502464108
O4	-1.6695604807	-2.5653269500	-0.4708374266
O5	0.6269750019	-0.5073752684	-1.0661618788
H6	0.5288150237	0.1884241558	-1.7336739153

$Re(CO)_5$-CH_3- $SeO_2(OH_2)$ (transition state)
$E_{elctronic}$= -3312.077484
E_{solv}= -0.0464542
ZPE= 67.343 kcal/mol
$\Delta H_{298.15}$= 13.2427 kcal/mol
$\Delta S_{vib\ 298.15}$= 75.018 cal/(mol K)
$\Delta S_{trans,rot\ 298.15}$= 39.515 cal/(mol K)

C1	0.0000000000	0.0000000000	0.0000000000
Se2	0.0000000000	0.0000000000	2.3900693319
O3	1.6798071606	0.0000000000	2.6747936700
H11	-1.0696985896	0.1335806793	0.0923257830
H12	0.4731722447	-0.9686108080	0.0923257830
H13	0.6245865390	0.8743093788	-0.1234666410
Re8	-0.4784067729	-0.6696838665	-2.3976267560
O14	-0.5446101614	1.5890726443	2.6747936700
C9	1.4850058584	-0.3730684811	-2.8029977656
O10	2.5813600936	-0.2069265646	-3.0428845619
O11	-1.0326520335	2.3748406923	-3.0428845619
C12	-0.8343708914	1.2838409974	-2.8029977656
O13	-1.0643923999	-1.4899588764	-5.3170357053
C14	-0.8433162133	-1.1804917789	-4.2379670899
O15	-3.5110705427	-1.0664054724	-1.6091719207
C16	-2.4203770872	-0.9261986410	-1.8958213746
O17	0.1295201831	-3.6671598696	-1.6091719207
C18	-0.0914598837	-2.5899236006	-1.8958213746
H15	2.2385001677	1.8432290771	3.1202585879
O16	1.9886989273	2.7838226011	3.0866357406
H17	1.0179233702	2.7151811070	3.1202585879

$Re(CO)5\text{-}O_2SeCH_3$
$E_{elctronic}$= -3312.156536
E_{solv}= -0.0273795
ZPE= 69.668 kcal/mol
$\Delta H_{298.15}$= 13.8415 kcal/mol
$\Delta S_{vib\ 298.15}$= 79.877 cal/(mol K)
$\Delta S_{trans,rot\ 298.15}$= 39.002 cal/(mol K)

C7	0.6390385808	1.2755266038	2.1484293134
Se1	-0.4740536308	-0.0808739301	1.2848555934
O2	-1.8933313498	0.7802496448	1.0276204038
Re8	-0.4622391392	-0.9929720399	-2.0397339327
C9	-2.2260483327	0.0152898112	-1.9522441148
O10	-3.2397775680	0.5227630727	-2.0079773922
O11	-1.7489632940	-3.3880848709	-0.4403253272
C12	-1.2755731347	-2.5086712263	-0.9829858123
O13	-1.4275073734	-2.3471620538	-4.6526100685
C14	-1.0680476255	-1.8421079538	-3.6874724927
O15	2.2899576452	-2.5456485118	-2.1470508692
C16	1.3043716058	-1.9858058928	-2.1067889289
O17	0.8114883757	1.3119433956	-3.8003436881
C18	0.3567649756	0.5087517709	-3.1409280713
H19	1.6576837190	0.9003865775	2.2391221946
H20	0.2076227426	1.4742594287	3.1306441462
H21	0.5864470089	2.1595219794	1.5136837329
O3	0.3680877823	-0.0279209268	-0.2706128488
H3	-1.3362694462	2.1945798743	-0.1232061045
O5	-0.6673380031	2.6198744133	-0.6959260522
H6	-0.0225978391	1.8997349940	-0.7772344606

Se oxidation TS, direct O-atom transfer TS.

Se1	0.0239215632	0.0765523997	0.0217399942
O2	0.0792116917	0.0775929866	1.6639115644
O3	1.7230443193	-0.0130642108	-0.5450570575
H4	1.9674809126	-0.9553190069	-0.7449659046
C5	-0.0789910595	1.9880860260	-0.4361504988
H6	0.7778569985	2.4538527731	0.0515356767
H7	-0.0322404657	2.0781497430	-1.5205227446
H8	-1.0243197570	2.3532041713	-0.0372816879
O9	-0.2805444237	-1.9206431258	-0.8198772594
I10	0.7694665424	-3.4974609660	-1.4441822032
O11	2.3694744234	-2.6106653563	-1.2369788326
O12	0.9188955813	-5.0242437029	-0.4381368216
O13	0.6883234876	-3.9657370104	-3.2148921436

Possible 1,2-methyl shift TS

Se1	0.2687278944	-0.1052740646	0.0142663935
O2	0.0089013861	0.2155844556	1.7862167233
H3	0.8497950525	0.4366490405	2.2224297673
O4	0.9397795518	1.2608028219	-0.5868686545
O5	-1.3450643761	-0.2072600288	-0.4261474590
C6	-0.3762682841	-2.3504987578	-0.6359424165
H7	-1.3528333645	-2.3490839924	-1.0936813923
H8	0.4908854964	-2.4406074336	-1.2787872773
H9	-0.2887329076	-2.7021816622	0.3857869321

Baeyer-Villiger Functionalization TS

Se1	-0.2218398077	-0.2091891474	-0.2095823901
O2	0.0273362132	0.2622984504	1.3391982467
O3	1.8484974697	-0.6020046745	-0.5548783365
H4	2.2537077862	-0.5696916327	0.3257830900
C5	-2.3531366422	-0.7953092049	0.0888733342
H6	-2.7279250742	-1.2033206166	-0.8426594412
H7	-2.4261590676	-1.4555668855	0.9450225121
H8	-2.6646975280	0.2294839793	0.2945180523
O9	-0.4107857895	-1.9914627454	-0.2952971937
I10	1.4941649201	-3.0713528944	-0.8702204953
O11	2.8999390086	-3.1976700378	0.2990931723
O12	0.7694981298	-4.7514012852	-0.8579063704
O13	2.1282011451	-2.8586271602	-2.5747154191

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